

## A comparative study of the orbital valency force field (OVFF) and the modified Urey-Bradley force field (MUBFF) models for the pentahalides of group V elements

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A comparative study of the orbital valency force field (OVFF) and the modified Urey-Bradley force field (MUBFF) models, as applied to a group of pentahalides, has been carried out. The OVFF model is found to be better suited than the MUBFF model in that in the former the use of angular coordinates has better theoretical justification, the least squares iterative calculation yields unique sets of force constants for all the pentahalides, and the agreement between the observed and the calculated frequencies is good.

### 1. INTRODUCTION

For the study of intramolecular force fields, several force field models have been put forward. Among the different force field models, the orbital valency force field (OVFF) (Heath & Linnett 1948, Tyson *et al* 1971) and the Urey-Bradley force field (UBFF) (Shimanouchi 1949) are widely used by different investigators. Both of these use the conventional bond-stretching force constants and the Urey-Bradley treatment of interactions between nonbonded atoms, but differ in their treatment of the angle coordinates. The UBFF uses the change of interbond angles as coordinates, while the OVFF uses the angles between ligand positions and the presumed positions of maximum orbital overlap. It was observed by Condrate & Nakamoto (1966), that the simple UBFF is not suitable for the pentahalides of group V elements. They found that the disparity between the calculated and the observed frequencies is mostly pronounced in the angle bending modes  $\nu_6$  and  $\nu_7$ . To improve the agreement, they had to introduce tentatively an additional angle-angle interaction constant  $H_{\alpha\beta}$  in the potential energy, which does not follow from the UBFF model. This model has been called the modified Urey-Bradley force field (MUBFF) model. The other model, namely, the OVFF has been used by Selig *et al* (1970) in calculations for  $\text{PF}_5$ ,  $\text{AsF}_5$  and  $\text{VF}_5$ . It has been observed by Kim *et al* (1968), for a series of symmetrical hexahalides, that the OVFF model is superior to the UBFF model, especially in the description of the bending modes. So far no comparison of the results of the normal coordinate calculation in both these models has been made from which the best suitable

model for the pentahalides can be chosen. Moreover, it is quite interesting to see whether the OVFF model is equally successful, as in hexahalides (Kim *et al* 1968), in describing the angle bending modes in the pentahalides. Based on these considerations we undertake here a comparative study of the OVFF and the MUBFF models as applied to the pentahalides of group V ( $\text{PF}_5$ ,  $\text{AsF}_5$ ,  $\text{VF}_5$ ,  $\text{PCl}_5$ ,  $\text{SbCl}_5$ ,  $\text{NbCl}_5$  and  $\text{PF}_2\text{Cl}_3$ ) using recent experimental observations. (Selig *et al* 1970, Hoskin *et al* 1967, Condrate & Nakamoto 1966, Werder *et al* 1967, Dieters & Holmes 1968).

The normal coordinate calculation of  $\text{PF}_5$ ,  $\text{AsF}_5$  and  $\text{VF}_5$  in the OVFF model has been done by Selig *et al* (1970). But no normal coordinate calculation in the MUBFF model for these fluorides is available, except for  $\text{PF}_5$  by Condrate & Nakamoto (1966). The assignment of one fundamental mode  $\nu_7$ , used by them is not supported by recent observations (Beattie *et al* 1969). So the evaluation of the force constants in the MUBFF model of this molecule along with those of  $\text{AsF}_5$  and  $\text{VF}_5$  is desirable. No OVFF calculation for the chlorides are available so far. Out of the four chlorides,  $\text{PCl}_5$ ,  $\text{SbCl}_5$ ,  $\text{NbCl}_5$  and  $\text{PF}_2\text{Cl}_3$ , only the force field calculation in the MUBFF for  $\text{PCl}_5$  and  $\text{SbCl}_5$  had been reported previously by Condrate & Nakamoto (1966). For comparison, the evaluation of the force constants of all the chlorides in the OVFF model, and that in the MUBFF model for  $\text{NbCl}_5$  and  $\text{PF}_2\text{Cl}_3$  is necessary and has been performed in this work. The results obtained from the two different force field calculations not only aid the choice of the better model, but also offer the opportunity to compare the values of the derived force constants which have the same meaning in both the models. It was also noted by Condrate & Nakamoto (1966) that the nonbonded interaction constants for  $\text{PCl}_5$  and  $\text{SbCl}_5$  can be fairly approximated by the Lennard-Jones (6-12) potential. We have examined the applicability of the L-J potential for nonbonded interaction in all the halides discussed here.

## 2. EXPERIMENTAL FREQUENCIES

The trigonal bipyramidal molecule of the types  $\text{XY}_3\text{Z}_2$  belongs to the symmetry group  $D_{3h}$ . Its twelve normal modes belong to the irreducible representations  $A_1'$ ,  $A_2''$ ,  $E'$ ,  $E''$ . Two frequencies occupy each of the  $A_1'$  and  $A_2''$  modes, and the occupancies of the representations  $E'$  and  $E''$  are 6 and 2 respectively, these being doubly degenerate.  $A_1'$ ,  $E'$  and  $E''$  are Raman active and species  $A_2''$  and  $E'$  are infrared active. The observed frequencies used in this work are given in table 1. For  $\text{PF}_5$ , the assignment of the fundamental frequencies by different investigators is consistent except for the lowest mode  $\nu_7$ . It was wrongly assigned by Griffith *et al* (1964) at  $300\text{ cm}^{-1}$  which later proved to be a difference band (Dieters & Holmes 1968). The latest assignment of  $\nu_7$  for this molecule is at  $175\text{ cm}^{-1}$  in the gas phase and made by Beattie *et al* (1969). For  $\text{AsF}_5$ , the latest experimental results are those of Hoskin & Lord (1967) and of Selig *et al*

(1970). The assignment of the fundamental frequencies of  $\text{AsF}_5$  by both the groups is in agreement except for the  $\nu_6$  mode which is both Raman and infrared active. Hoskin & Lord (1967) assigned the  $\nu_6$  at  $366 \text{ cm}^{-1}$  obtained from the Raman studies and also listed an infrared  $P$  and  $R$  branch of this mode at  $375 \text{ cm}^{-1}$  and at  $369 \text{ cm}^{-1}$  respectively. However, later investigations of Selig *et al* (1970) failed to locate any Raman transition at  $366 \text{ cm}^{-1}$ , but confirmed the earlier studies in the infrared. Selig *et al* assigned  $\nu_6$  at  $372 \text{ cm}^{-1}$  based on the infrared data, and this has been used in this work. The fundamental frequencies of  $\text{VF}_5$  are those given by Selig *et al* (1970). The frequencies of  $\text{PCl}_5$  and  $\text{SbCl}_5$ , used by Condrate & Nakamoto (1966), have also been used in the present work. The frequencies of  $\text{PF}_2\text{Cl}_3$  are those given by Griffiths *et al* (1964). The latest infrared data of  $\text{NbCl}_5$  are those given by Wercer *et al* (1967). No recent Raman data for this compound in the gas phase are available. The frequencies of the species  $A_1'$  and  $E''$  are taken from the earlier Raman data of Gaunt & Aniscough (1957).

### 3. THEORY AND CALCULATION

#### *The modified Urey-Bradley force field (MUBFF) model*

The MUBFF used by Condrate & Nakamoto (1966) has also been used in this work. For the sake of completeness we give below the expression for the potential energy  $V$ .

$$\begin{aligned}
 V = & \sum_i [K_r' r(\Delta r_i) + \frac{1}{2} K_r (\Delta r_i)^2] + \sum_i [K_d' d(\Delta d_i) + \frac{1}{2} K_d (\Delta d_i)^2] \\
 & + \sum_{i < j} [H'_\alpha r_\alpha^2 (\Delta \alpha_{ij}) + \frac{1}{2} H_\alpha (r_\alpha \Delta \alpha_{ij})^2] + \sum_{i < j} [H'_\beta r_\beta^2 (\Delta \beta_{ij}) + \frac{1}{2} H_\beta (r_\beta \Delta \beta_{ij})^2] \\
 & + \sum_{i < j} [F'_{rr} r r (\Delta q_{ij}) + \frac{1}{2} F_{rr} (\Delta q_{ij})^2] + \sum_{k < j} [F'_{ar} a r (\Delta q_{jk}) + \frac{1}{2} F_{ar} (\Delta q_{jk})^2] \\
 & + \sum_{k \neq i < j} [H_{\alpha\beta} (r_\alpha \Delta \alpha_{ij})(r_\beta \Delta \beta_{ik})].
 \end{aligned} \tag{1}$$

The symbols  $K$ ,  $H$ ,  $F$  and  $H_{\alpha\beta}$  represent the stretching, bending, repulsive and angle-angle interaction constants respectively.  $K'$  and  $H'$  can be represented in terms of  $F'$ , the latter being taken as  $-0.1 F$  (Condrate *et al* 1966).  $r$ ,  $d$ ,  $\alpha$  and  $\beta$  denote, respectively, the equatorial bond length, axial bond length, in-plane angle and axial angle.  $q$ 's denote the nonbonded distances. For the calculation of vibrational frequencies, Wilson's  $F$ - $G$ -matrix method has been used. The symmetry coordinates given by Condrate & Nakamoto (1966) are used in the MUBFF model calculation.

#### *Orbital valency force field*

The potential energy in the OVFF model can be written in the following way (Tyson *et al* 1971)

$$\begin{aligned}
2V = & \Sigma[2K'_r r(\Delta r_t) + K_r(\Delta r_t)^2] + \Sigma[2K'_a d(\Delta d_t) + K_a(\Delta d_t)^2] \\
& + \Sigma_{i < j} [2F'_{rr} q_{rr}(\Delta q_{ij}) + F_{rr}(\Delta q_{ij})^2] + \Sigma_{k < j} [2F'_{ar} q_{ar}(\Delta q_{jk}) + F_{ar}(\Delta q_{jk})^2] \\
& + Dr^2 \sum_{i=1}^3 \gamma_i^2. \quad \dots \quad (2)
\end{aligned}$$

The force constants of this model have the same meaning as those of the MUBFF model except for the angle constant  $D$ . In the OVFF model the angular part of the potential energy is expressed not in terms of the interbond angles  $\alpha$  and  $\beta$ , but in terms of angles  $\gamma_i$  between the actual position of the ligands and the direction where the  $i$ -th orbital is centered when the orbital energy is minimized. When all the ligands are same we have a single angle constant  $D$ . In this case we have put the ratio of the axial and equatorial bond lengths as unity, following Selig *et al* (1970). They have shown that this approximation introduces an error of the order of 1% in the calculated values of the frequencies. When the axial atoms are different from the equatorial atoms, we have used two angle constants  $D$  and  $D'$ . The summation over the angle coordinates in eq. (2) associated with the constants  $D$  and  $D'$  run respectively over the three equatorial and the two axial ligand positions. The choice of two independent constants  $D$  and  $D'$  instead of a single constant is dictated by the fact that the axial ligands are different from the equatorial ones. This choice does not violate the symmetry of normal modes and gives zero frequencies of translation and rotation, which, of course, is also maintained with the choice of one constant only. Since in this case, we are dealing with two different species of ligand atoms, it is better to use  $F'_{ar}$  as an adjustable parameter, instead of preassigning a value  $-0.1 F_{ar}$  to it as was done in the previous case. We now have a set of seven force constants  $K_r$ ,  $K_a$ ,  $F_{rr}$ ,  $F_{ar}$ ,  $D$ ,  $D'$  and  $F'_{ar}$ . Further the actual values of the equatorial and the axial bond lengths have been used to evaluate the force constant matrix  $F$ .

If the potential energy is expressed in the mass weighted cartesian coordinates, the frequencies are obtained by diagonalizing the matrix  $M^{-\frac{1}{2}} F M^{-\frac{1}{2}}$ , where  $M$  is a diagonal matrix containing the masses of the respective atoms.

The iterative least squares fit technique of Aldous & Mills (1963) has been used in the calculation. The weight assigned to each observed frequency is equal to  $1/\lambda_i^2$  (Aldous & Mills 1963) where  $\lambda_i$  is related to the frequency ( $\text{cm}^{-1}$ ) by the following expression

$$\lambda_i = 4\pi^2 c^2 \nu_i^2. \quad \dots$$

The masses used in the present calculation are based on O<sup>16</sup> unit.

## 4. RESULTS AND DISCUSSION

*Fluorides*

The differences between the observed frequencies and the corresponding calculated values in the MUBFF model for  $\text{PF}_5$ ,  $\text{AsF}_5$  and  $\text{VF}_5$  are given in table 2. In the case of  $\text{PF}_5$  and  $\text{AsF}_5$ , the two Coriolis zeta constants ( $\zeta_5$  and  $\zeta_6$ ) have been included as observables in the iterative least squares fit. The corresponding Jacobian for the Coriolis constants is given by Mills (1960). The value of  $\zeta_7$  is calculated from the derived force constants and they are found to satisfy strictly the  $\zeta$ -sum rule  $\zeta_5 + \zeta_6 + \zeta_7 = 1$  (Lord & Merrifield 1952). For each of the fluorides, the force constants, instead of converging on to a unique set of values, are found to oscillate within certain ranges as the iteration continues. Out of these many sets of force constants, we choose the one which minimizes the sum of the weighted squares of errors. For comparison, the difference between the observed and the calculated frequencies of Selig *et al* (1970) for these compounds in the OVFF model is also given in table 2. However, to test the convergence, we repeated the calculation for the fluorides in the OVFF model. It is found that the convergence is rapid, and there is no oscillation as in the MUBFF case.

Table 1. Values of the observed fundamental frequencies ( $\text{cm}^{-1}$ ) and bond length ( $\text{\AA}$ )

Species		$\text{PF}_5$	$\text{AsF}_5$	$\text{VF}_5$	$\text{SbCl}_5$	$\text{NbCl}_5$	$\text{PCl}_5$	$\text{PF}_2\text{Cl}_3$
$A_1'$	$\nu_1$	817	734	718	356	412	394	633
	$\nu_2$	640	644	608	307	355	264	387
$A_2''$	$\nu_3$	945	784	784	387	396	465	867
	$\nu_4$	576	400	331	154	126	299	328
$E'$	$\nu_5$	1026	811	810	398	444	592	625
	$\nu_6$	533	372	282	172	159	273	404
	$\nu_7$	175	130	109	74	99	100	122
$E''$	$\nu_8$	514	386	336	165	106	282	357
Equatorial bond length		1.534 <sup>e</sup>	1.656 <sup>f</sup>	1.8 <sup>g</sup>	2.31 <sup>c</sup>	2.29 <sup>d</sup>	2.04 <sup>e</sup>	2.04 <sup>h</sup>
Axial bond length		1.577	1.711	1.8	2.43	2.29	2.19	1.55

The observed Coriolis constants  $\zeta_5$  and  $\zeta_6$  of  $\text{PF}_5$  are  $0.77 \pm 0.05$ ,  $0.24 \pm 0.05^a$ , and of  $\text{AsF}_5$   $0.31 \pm 0.05$ ,  $0.80 \pm 0.10^b$ .

<sup>a</sup>. Selig *et al* (1970) <sup>b</sup>. Hoskins & Lord (1967) <sup>c</sup>. Condrate & Nakamoto (1966) <sup>d</sup>. Skinner & Sutton (1940) <sup>e</sup>. Hanson & Bartell (1965) <sup>f</sup>. Clippard & Bartell (1970) <sup>g</sup>. Assumed <sup>h</sup>. Griffiths *et al* (1964).

Table 2. The differences between the observed and calculated frequencies ( $\text{cm}^{-1}$ ) and Coriolis constants in the MUBFF and OVFF models for  $\text{PF}_5$ ,  $\text{AsF}_5$  and  $\text{VF}_5$

		$\text{PF}_5$		$\text{AsF}_5$		$\text{VF}_5$	
		MUBFF (Present work)	OVFF (Selig <i>et al</i> 1970)	MUBFF (Present work)	OVFF (Selig <i>et al</i> 1970)	MUBFF (Present work)	OVFF (Selig <i>et al</i> 1970)
Frequency	$\nu_1$	- 6	-24	-15	- 7	- 6	-14
	$\nu_2$	9	27	11	30	7	11
	$\nu_3$	- 4	-15	3	-15	- 2	- 7
	$\nu_4$	30	15	24	14	6	5
	$\nu_5$	- 1	- 9	1	-18	- 1	5
	$\nu_6$	1	7	3	5	1	- 4
	$\nu_7$	2	0	5	0	2	0
	$\nu_8$	-20	- 8	-16	-14	0	2
Coriolis	$\zeta_5$	0.15	0.20	0.02	-0.25		
Constant	$\zeta_0$	0.02	-0.15	0.38	0.0		

### Chlorides

We have considered the compounds  $\text{SbCl}_5$ ,  $\text{PCl}_5$ ,  $\text{NbCl}_5$  and  $\text{PF}_2\text{Cl}_3$  for our calculation. The OVFF model frequencies for all these molecules, not available in the literature so far, have been calculated and their differences from the observed values are presented in table 3. The MUBFF model frequencies are available only for the compounds  $\text{PCl}_5$  and  $\text{SbCl}_5$  (Condrate & Nakamoto 1966). We found that the OVFF model gives rapid convergence in all the cases. The question of convergence has not been discussed by Condrate & Nakamoto (1966) in their MUBFF calculations, and further, in their least squares fit analysis, they have not weighted their input frequencies properly to account for the errors in the observations. For these reasons, we performed a separate MUBFF calculation for all the chlorides, including the ones treated by Condrate & Nakamoto. We have listed the deviations of our values from the observed ones in table 3. Convergence was attained in all cases excepting  $\text{NbCl}_5$ , for which the criterion of minimizing the sum of the weighted squares of errors was set.

We find that in all the halides, the agreement between all our calculated OVFF frequencies and the observed ones is reasonably good. The particularly gratifying features of the OVFF model is that it gives nice agreement with the observed frequencies for the  $\nu_6$  and  $\nu_7$  modes, which does not emerge in a purely

Table 3 : The differences between the observed and calculated frequencies ( $\text{cm}^{-1}$ ) in the MUBFF and OVFF models for  $\text{SbCl}_5$ ,  $\text{PCl}_5$ ,  $\text{NbCl}_5$  and  $\text{PF}_5\text{Cl}_3$ .

Frequency $\nu_i$	$\text{SbCl}_5$		$\text{PCl}_5$		$\text{NbCl}_5$		$\text{PF}_5\text{Cl}_3$	
	MUBFF	OVFF	MUBFF	OVFF	MUBFF	OVFF	MUBFF	OVFF
$\nu_1$	0 ( 3)	13	-3 ( 0)	- 8	30	14	2	3
$\nu_2$	2 ( 0)	9	4 ( 3)	5	38	38	0	- 7
$\nu_3$	-3 ( 3)	- 9	-5 (-5)	- 5	-27	-27	- 2	2
$\nu_4$	-1 (-2)	-11	-3 (-4)	- 3	7	-10	11	- 7
$\nu_5$	0 (-4)	- 9	0 ( 4)	- 2	- 9	-11	0	10
$\nu_6$	0 ( 0)	15	0 (-5)	- 8	-11	6	0	- 4
$\nu_7$	0 ( 0)	2	0 ( 0)	0	7	2	0	1
$\nu_8$	-1 ( 2)	2	4 ( 5)	16	-17	4	-11	9

The quantities within the parenthesis denote the difference between the observed and the calculated frequencies of Condrate & Nakamoto (1966).

Urey-Bradley treatment of the force field. The MUBFF model was designed primarily to take care of these modes, but this model contains an angle-angle interaction constant  $H_{\alpha\beta}$ , whose presence, from the point of view of non-bonded interaction between atoms, is rather arbitrary. Moreover, due to lack of convergence in the least squares iterative analysis for  $\text{PF}_5$ ,  $\text{AsF}_5$ ,  $\text{VF}_5$  and  $\text{NbCl}_5$  in the MUBFF model, the reported differences between the observed and calculated frequencies do not possess any unique meaning because they are tentatively chosen out of a number of possible values. The same difficulty has also been previously encountered in the normal coordinate analysis in the other force field model (Aldous & Mills 1963). Thus, although the MUBFF gives marginally better agreement with the observed frequencies in general, the OVFF model is certainly more desirable because it displays convergence in all the cases studied so far, and because of its sound and consistent theoretical basis.

#### Force Constants

The desired force constants for the fluorides in the MUBFF are given in table 4. The force constants for the same compounds in the OVFF model by Selig *et al* (1970) are also given there for comparison. Since in the OVFF model, only five constants are used to explain eight observables, the evaluation of the standard deviations of the derived force constants is desirable. The force constants and their corresponding standard deviation for these compounds in the OVFF model, as evaluated by us, are also given in table 4. The values of the force constants, for the chlorides, namely  $\text{PCl}_5$ ,  $\text{SbCl}_5$ ,  $\text{NbCl}_5$  and  $\text{PF}_2\text{Cl}_3$ , in the MUBFF and in the OVFF model, are given in table 5. It is to be noted that our converged and properly weighted sets of force constants for  $\text{SbCl}_5$  in the MUBF are different from the values quoted by Condrate & Nakamoto (1966). For  $\text{PCl}_5$ , both the sets are in reasonable agreement.

Since the OVFF model gives convergence for all the pentahalides, the derived force constants are unique. On the contrary, lack of convergence and the oscillatory nature in the iteration for  $\text{PF}_5$ ,  $\text{AsF}_5$ ,  $\text{VF}_5$  and  $\text{NbCl}_5$  in the MUBFF model makes it difficult to ascertain the uniqueness of the force constants in this approach. We may notice certain systematics and patterns in the values of the calculated force constants. The stretching force constants of the individual species in both the models are comparable and it is found that the equatorial stretching force constant is always greater than the axial one. This means, by Badger's rule (Badger 1934), that the axial bond length is greater than the equatorial one which is supported by the evidence obtained from electron diffraction and X-ray data (Hanson & Bartell 1965, Clippard & Bartell 1970). The bond stretching force constants containing fluorine atoms are much larger than those involving chlorine atoms. Both the equatorial and the axial stretching force constants for the chlorides follow the sequence  $\text{Nb-Cl} > \text{Sb-Cl} > \text{P-Cl}$ . This is consistent with the difference in electronegativity between the bonded atoms.



Table 4 : Force constants of the pentafluorides in MUBFF and OVFF model.

Force constants (milli dyne/Å)	PF <sub>5</sub>		AsF <sub>5</sub>		VF <sub>5</sub>	
	MUBFF	OVFF	MUBFF	OVFF	MUBFF	OVFF
$K_r$	5.256	5.569±0.435 ( 5.47)	4.966	5.285±0.452 ( 5.20)	4.422	4.278±0.192 ( 4.28)
$F_{rr}$	0.322	-0.184±0.176 (-0.11)	0.364	-0.271±0.166 (-0.22)	0.279	0.192±0.058 ( 0.19)
$H_a(D)$	0.086	0.55 ±0.169 ( 0.48)	0.005	0.467±0.161 ( 0.41)	-0.05	-0.029±0.05 (-0.03)
$K_a$	3.795	3.961±0.318 ( 3.93)	4.243	4.26 ±0.399 ( 4.21)	3.675	3.644±0.144 ( 3.64)
$F_{ar}$	0.901	1.368±0.124 ( 1.36)	0.20	0.671±0.121 ( 0.72)	0.434	0.663±0.042 ( 0.66)
$H_{\rho}(D')$	0.415		0.406		0.123	
$H_{a\theta}$	0.167		0.113		0.020	

<sup>a</sup>The bracketed quantities are the force constants reported by Selig *et al* (1970).

Table 5 : Force constants of the pentachlorides in the MUBFF and OVFF model.

Force constants (milli dyne/Å)	SbCl <sub>5</sub>		PCl <sub>5</sub>		NbCl <sub>5</sub>		PF <sub>2</sub> Cl <sub>3</sub>	
	MUBFF	OVFF	MUBFF	OVFF	MUBFF	OVFF	MUBFF	OVFF
$K_r$	2.172 (2.20)	2.293±0.333	2.187 (2.10)	2.217±0.195	2.618	2.629±0.424	2.282	2.266
$F_{rr}$	0.154 (0.08)	-0.061±0.114	0.108 (0.10)	0.003±0.071	0.132	0.207±0.103	0.104	0.183
$H_a(D)$	0.036 (0.06)	0.166±0.106	0.055 (0.07)	0.215±0.067	0.102	0.119±0.064	0.084	0.130
$K_a$	1.919 (1.83)	1.758±0.234	0.966 (1.00)	1.064±0.094	2.065	2.038±0.290	3.491	3.412
$F_{ar}$	0.016 (0.13)	0.201±0.073	0.534 (0.55)	0.658±0.049	0.028	0.05 ±0.045	0.813	0.881
$H_{\rho}(D')$	0.150 (0.085)		0.163 (0.15)		0.075		0.112	0.157
$H_{a\theta}$	0.043 (0.043)		0.059 (0.07)		-0.002		0.074	-0.127 <sup>b</sup>

<sup>a</sup>The bracketed quantities are the force constants reported by Condrate *et al* (1966)

<sup>b</sup>This quantity denotes  $F'_{ar}$  (See text)

If the repulsion between the fluorine atoms and that between the chlorine atoms are purely of a Van der Waal's type, the values of the constants  $F$  can be compared with the force constants derived from Lennard-Jones (6-12) potential of Ne-Ne and Ar-Ar respectively (Kihara 1958). For fluorides, there is a marked difference between the value found from an OVFF calculation and the value obtained from consideration of (Ne-Ne) L-J potential as displayed in figure 1. This difference suggests that besides the dispersion forces extra repulsive forces are present. The fact that bonds containing fluorine atoms are usually ionic in character, means that the coulomb force, besides the dispersion force, should be taken into account as suggested in the cases of transition metal hexafluorides (Kim *et al* 1968) and transition metal oxoanions (Krebs & Muller 1967). This seems to

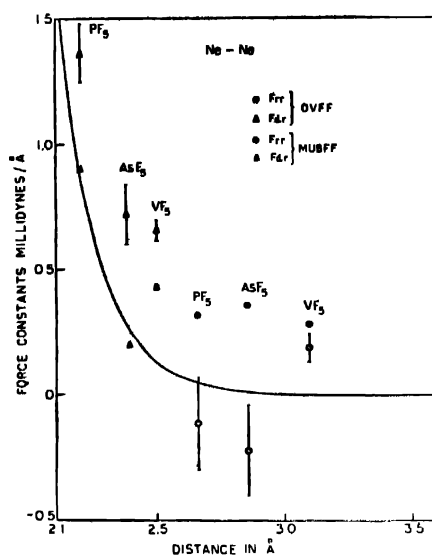


Fig. 1.  $F_{rr}$  repulsive force constants versus distance. The theoretical curve is drawn from the Lennard-Jones 6-12 potential for Ne...Ne.

be quite plausible in view of the fact that the deviation is very much pronounced in the values of  $F_{dr}$  where the nonbonded distance is quite small. The force constants  $F_{dr}$  for  $PF_5$  and  $AsF_5$  obtained on the MUBFF model, are in reasonable agreement with those found in the L-J calculations. Since there is no fundamental difference in the treatment of nonbonded interaction in the two models, this agreement in the MUBFF model is against the idea of additional coulomb interaction. However, the superiority of the MUBFF model in this respect is more apparent than real, because of the nonunique character of the derived force constants, as mentioned earlier. The negative sign of  $F_{rr}$  for  $PF_5$  and  $AsF_5$ , as obtained from the OVFF model, cannot be explained in terms of nonbonded interaction alone, which requires the value of  $F_{rr}$  to be positive. However, the large uncertainty

in the values of  $F_{rr}$  for  $\text{PF}_5$  and  $\text{AsF}_5$  show that the values are not well determined with the available informations. In the case of chlorides, these force constants are consistent in both the MUBFF and the OVFF models and are fairly approximated by the L-J potential within the limit of calculated uncertainty as shown in figure 2. From this we conclude that the dispersion force is mainly responsible for the nonbonded interaction in the case of these chlorides. The coulomb interaction is quite small because the nonbonded distances between Cl-Cl atoms are comparatively large and the ionicity of the bonds containing the chlorine atom is usually smaller than that of the bonds containing fluorine atoms. The angle constants from the two different models cannot be compared with each other due to their different meanings.

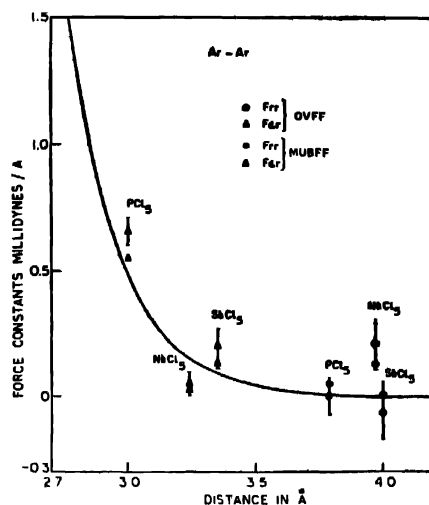


Fig. 2. Cl...Cl repulsive force constants versus distance. The theoretical curve is drawn from the Lennard-Jones potential 6-12 for Ar...Ar.

## 5. CONCLUSION

In this paper, the force constants of  $\text{PF}_5$ ,  $\text{AsF}_5$ ,  $\text{VF}_5$ ,  $\text{NbCl}_5$  and  $\text{PF}_2\text{Cl}_3$  have been evaluated in the MUBFF model. The reevaluation of the force constants of  $\text{PCl}_5$  and  $\text{SbCl}_5$  completes the list of halides discussed. The force constants of the  $\text{PCl}_5$ ,  $\text{SbCl}_5$ ,  $\text{NbCl}_5$  and  $\text{PF}_2\text{Cl}_3$  in the OVFF model, hitherto not available, are presented. The force constants in the OVFF model for the remaining fluorides,  $\text{PF}_5$ ,  $\text{AsF}_5$  and  $\text{VF}_5$ , are given by Selig *et al* (1970) and have also been evaluated by us. The convergence in the iteration and hence the unique set of force constants for all the pentahalides, and the reasonable agreement between the observed and the calculated frequencies in the OVFF model, favour its use over the modified Urey-Bradley model. Moreover, the use of angle coordinates in a way which is more consistent with the chemical theory of bonding (Heath & Linnett 1948), gives additional support to this model.

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